NON-COULOMB CENTRAL FIELD FOR POTASSIUM ATOM

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ABSTRACT. The potential field for KII is obtained. Out of the four methods described it is shown that for calculation of line intensities or term values of the atomic spectrum, empirical field obtained from Prokofjew method is the best. For heavy atoms a simple method based on Fermi statistical field is given, where the field for the neutral atom is altered due to the removal of the optical electron.

To calculate line intensities, etc., of potassium atom from the Schroedinger equation, a potential function known at every point is required. Hartree's (1934), self-consistent field is available, but apart from the huge labour involved in such computation, Hartree (1927-28) has pointed out that the self-consistent field can be used best only when charge distribution is required explicitly, *e.g.*, in X-Ray scattering work. For calculation of line intensities some other empirical potential field is to be used. In the elucidation of atomic spectra the field required is the one acting on the outermost optical electron due to the rest of the atom, *i.e.*, the ion.* Fermi and Thomas have given a field for a heavy neutral atom from statistical considerations. The field due to the ion can be deduced from that of the neutral atom as will be shown below.

Fermi (1928), and Condon and Shortly (1935), have shown that for a fairly continuous charge distribution due to electrons in a heavy atom (Z), potential field V is obtained from :

$$\nabla^2 V = 4\pi e \cdot \frac{8\pi}{3h^3}(2mc)V^{\frac{3}{2}}.$$

Put

$$V = \frac{Ze}{r}\chi(r), \text{ and } r = xb,$$

where

$$b = \frac{1}{2}\left(\frac{3\pi}{4}\right)^{\frac{2}{3}} \frac{a}{Z^{\frac{1}{3}}}$$

and a is the Bohr radius, and other constants are obvious.
The equation reduces to

$$x^{\frac{1}{2}} \frac{d^2\chi}{dx^2} = \chi^{\frac{3}{2}}$$

which has been solved mechanically, by Bush and Caldwell (1931), for neutral atoms, *i.e.*, under the boundary conditions $\chi = 1$ and 0, at $\rho = 0$ and ∞ respectively. From tables given by them, Z (effective) $= \chi Z$ can be calculated for any neutral atom (Z). To get the field for the ion, the method employed by Fermi (1928), was to get the statistical field for the neutral atom of atomic number $(Z-1)$, and to impose upon it the field due to an additional proton at the centre.

* Strictly speaking the field required in any calculation will be the one obtained after a disturbance has been imposed upon the true ion field by the optical electron. Field II and III out of the four are most appropriate in this respect.

Thus for ion of atom Z, the Z_{eff} at distance r is give by $(Z-1)\chi(r)+1$. But this added proton sensibly closes up the distribution of the electrons. Best way appears to be to subtract the contribution of the outermost negative electron from the Z_{eff} of neutral atom. Any departure of the field obtained in this way from the true ionic field, as given by Baker (1930), will in fact represent to a close approximation the disturbance of that field by the optical electron for any particular calculation. This electron subtraction method is explained below with potassium as an example.

From the statistical calculation of Fermi the number of electrons per c.c., in a field given by $Z_{eff}=\chi Z$ in heavy neutral atom, is

$$n=\frac{8\pi}{3h^3}\left(2mc\,\frac{\chi Zc}{r}\right)^{\frac{3}{2}}$$

Number of electrons in a shell of thickness dr of radius r is

$$4\pi r^2\,\frac{8\pi}{3h^3}\,(2mc^2\chi Z/r)^{\frac{3}{2}}dr.$$

Putting $r=\rho a$, we have number of electrons in a shell extending from ρ_1 to ρ_2 as

$$\int_{\rho_1}^{\rho_2}(2mc^2\chi Z/\rho a)^{\frac{3}{2}}(8\pi/3h^3)4\pi\rho^2a^3d\rho$$

which integral reduces to Z if limits are from o to ∞, as it should. Substituting for the constants the integral becomes

$$1.195\int_{\rho_1}^{\rho_2}(\chi Z)^{\frac{3}{2}}\rho^{\frac{1}{2}}d\rho.$$

Now, by drawing a graph between $(\chi Z)^{\frac{3}{2}}\rho^{\frac{1}{2}}$ and ρ, one can find the region which contains the outermost electron. Thus, from the relation

$$1.195\int_{\rho_{ion}}^{\rho\infty}(\chi Z)^{\frac{3}{2}}\rho^{\frac{1}{2}}d\rho=1$$

and integrating graphically (at very large ρ asymptotic $\chi Z=e^{k\rho}$ can be used) the radius ρ_{ion} can be determined. For potassium atom $\rho_{ion}=3.78$, removal of this negative charge means that we must add to the previous χZ the magnitude of its effect. Knowing that potential inside a charged spherical shell of radius R and charge Q is equal to Q/R, we have for all points at $\rho<\rho_{ion}$, contribution towards potential as

$$\int_{\rho_{ion}}^{\rho=\infty}\frac{de}{\rho a}=\frac{1.195e}{a}\int_{\rho_{ion}}^{\rho_\infty}\frac{(\chi Z)^{\frac{3}{2}}\rho^{\frac{1}{2}}}{\rho}\,d\rho$$

and since $V(\rho)=\frac{e}{\rho a}\cdot Z_{eff}$, contribution towards Z_{eff} for all points at $\rho<\rho_{ion}$ is

$$1.195\rho\int_{\rho_{ion}}^{\rho_\infty}\frac{(\chi Z)^{\frac{3}{2}}}{\rho^{\frac{1}{2}}}\,d\rho=\frac{\rho}{\rho_a}$$

From graphical integration, $\rho_a=5.424$ for potassium atom. For points at $\rho>\rho_{ion}$, contribution towards Z_{eff} is made of two parts, (*i*) due to charge lying

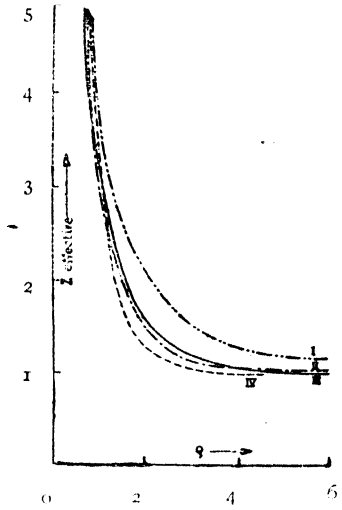
beyond ρ, and (*ii*) due to charge lying between ρ_{ion} and ρ which can be supposed to be placed at the centre. These are therefore

$$\rho \times 1.195 \int_{\rho}^{\rho_\infty} \frac{(\chi Z)^{\frac{3}{2}}}{\rho^{\frac{1}{2}}} d\rho, \text{ and } 1.195 \int_{\rho_{ion}}^{\rho} (\chi Z)^{\frac{3}{2}} \rho^{\frac{1}{2}} d\rho$$

Thus the required field is given by

For $\rho < \rho_{ion}$; $Z_{eff} = \chi Z + \frac{\rho}{\rho_a}$.

For $\rho > \rho_{ion}$; $Z_{eff} = \chi Z + 1.195\rho \int_{\rho}^{\rho_\infty} \frac{(\chi Z)^{\frac{3}{2}}}{\rho^{\frac{1}{2}}} d\rho + 1.195 \int_{\rho_{ion}}^{\rho} (\chi Z)^{\frac{3}{2}} \rho^{\frac{1}{2}} d\rho$.



I Statistical Proton addition.
II. Statistical Electron Subtraction.
III. Empirical Prokofjew method.
IV. Hartree Self-consistent method.

The results are given in the accompanying graph and Table II.

The statistical method being applicable only to heavy atoms, another method using experimentally observed term values of the neutral atom has been given by Sugiura (1927), and Prokofjew (1929) based upon simple Bohr-Sommerfeld theory. A useful form of the quantum condition obtained by Kramers is

$$n - k = \frac{\sqrt{2}}{\pi} \int_{\rho_{min}}^{\rho_{max}} \sqrt{-\tfrac{1}{2}\frac{\nu}{R}\rho^2 - \tfrac{1}{2}k^2 + Q(\rho)} \; \frac{d\rho}{\rho}$$

where

$$Q = \rho Z_{eff}, \qquad \text{and} \quad \rho = \frac{r}{a}.$$

ρ_{max} and ρ_{min} are the boundaries of the N_k orbit and are in fact the limits in which the integral has a sense. ρ_{max} and ρ_{min} are the roots of the expression under the square root when equated to zero. Sugiura and Prokofjew calculated the field function Q for sodium atom employing the Brillouin-Kramers approximation, *viz.*, that of replacing k by $k - \frac{1}{2}$. Prokofjew following an algebraic method got different expressions for Q in different regions. For each term the integration was carried out portion by portion in the region where it was valid, ρ_{max} and ρ_{min} being the higher root and the lower root respectively of corresponding equations. The algebraic method of Prokofjew is more sensitive and gives the results in a more useful form than the graphical method of Sugiura.

Hartree (*loc. cit.*) has shown that as far as we can picture an orbit corresponding to a given solution of the wave equation its angular momentum is defined by $\sqrt{l(l+1)}$ in place of k. Thus the quantum condition becomes

$$n - \sqrt{l(l+1)} = \frac{\sqrt{2}}{\pi}\int_{\rho_{min}}^{\rho_{max}} \sqrt{-\tfrac{1}{2}\frac{\nu}{R}\rho^2 - \tfrac{1}{2}l(l+1) + Q}\ \frac{d\rho}{\rho} \qquad \ldots (1)$$

As an example the field Q for potassium has been obtained below. Table I gives ν/R against various N_K values. Orbits marked * were actually used in the evaluation of the field in the order shown :

TABLE I

N_k	ν/R	N_k	ν/R	N_k	ν/R	N_k	ν/R
4.*1_1	265.6	4_3	.06933	6_3	.03015	8_3	.01666
2_1	—	4_4	.06277	6_4	.02786	1.*8_4	.01563
5.*2_2	21.73	5_1	.1274	7_1	.04313	9_1	.02149
3_1	—	5_2	.09385	7_2	.03505	9_2	.01882
6.*3_2	1.254	5_3	.04393	7_3	.02193	9_3	.01306
3.*3_3	1.230	5_4	.04014	7_4	.02045	10_1	.01633
4_1	.319	6_1	.06883	8_1	.02952	10_2	.01455
4_2	.2005	6_2	.05474	8_2	.02533	2.*10_3	.01053

Field Q is given below against ρ. As this field is based upon actual experimental results, it is the factual field and requires no extra corrections :

Orbit used.	ρ	Q
		ρ
1	∞ to 6.31	
2	6.31 to 1.90	$0.068\ \rho^2 + .1418\ \rho + 2.708$
3	1.90 to 1.106	$0.1595\ \rho^2 - .2078\ \rho + 3.0406$
6	1.106 to .5111	$0.6059\ \rho^2 - 1.1942\ \rho + 3.586$
6	.5111 to .4412	$-10.0\ \rho^2 + 9.647\ \rho + .806$
5	.4412 to .1053	$-12.1\ \rho^2 + 11.503\ \rho + .3951$
4	.1053 to 0.0	$-47.7\ \rho^2 + 19.00\ \rho$

Test for such work is to see if equation I is satisfied for any term not already used in the evaluation of Q. Taking the term 10_2 we have L.H.S. = 8.59 and computed R.H.S. = 8.60, the integral having a sense from $\rho = .0624$ to $\rho = 136.46$, *i.e.*, using up all the seven expressions which shows that method has not gone wrong anywhere.

The soft X-ray levels 2_1 and 3_1 which have not been experimentally determined are foretold by this field to be 26.41 end 2.72 respectively. Hartree's corresponding values are 26.68 and 3.084. Bearing in mind that the polarization corrections to be applied to Hartree values are negative, these results appear to be correct.

CONCLUSION

For calculation of line intensities, etc., empirical fields based upon experimental observation are best. The empirical method given by Prokofjew followed here for potassium is better than those given by Sugiura and others. For heavy atoms this field can be easily obtained by the electron subtraction method from

Fermi-Thomas statistical field for neutral atoms. Z_{eff} for potassium is tabulated against ρ in Table II from different methods.

TABLE II

ρ	Z effective			
	I. Proton addition.	II. Electron subtraction	III. Prokofjew.	IV. Self-consistent
0.0	19.0	19.0	19.0	19.0
0.02	18.1	17.9	18.046	17.576
0.04	17.2	16.9	17.092	16.346
0.06	16.4	16.2	16.138	15.316
0.08	15.5	15.0	15.184	14.433
0.1	14.5	14.0	14.230	13.652
0.2	11.2	11.0	11.039	10.564
0.3	9.2	8.8	9.190	8.444
0.4	7.8	7.3	7.651	7.054
0.5	6.7	6.2	6.259	6.094
0.6	5.8	5.3	5.147	5.353
0.7	5.2	4.5	4.353	4.722
0.8	4.7	4.0	3.773	4.162
0.9	4 2	3.5	3.326	3.660
1.0	3.9	3.1	2.998	3.218
1.2	3.3	2.6	2.517	2.504
1.4	2.8	2.2	2.188	1.997
1.6	2.5	1.9	1.947	1.650
1.8	2.3	1.7	1.769	1.420
2.0	2 1	1.5	1.628	1.270
3.0	1.5	1.13	1.248	1.028
4.0	1.3	1.07	1.091	1.002
5.0	1.2	1 05	1.023	1.000
6.0	1.15	1.04	1.001	,,
7.0	1.10	1.03	1.000	,,
8.0	1.05	1.02	,,	,,
9.0	1.02	1.01	,,	,,
10.0	1.02	1.0	,,	,,

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